# Reactions of *n*-$Bu_2SnO$ and (*n*-$Bu_3Sn)_2O$ with 1,1,2,3,3-Pentamethyltrimethylene Phosphinic Acid: Synthesis and X-ray Crystal Structures of a Novel Spirocyclic Coordination Polymer and a 16-Membered Inorganic Macrocycle

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The reactions of the sterically hindered phosphinic acid 1,1,2,3,3-pentamethyltrimethylene phosphinic acid [*cyc*P(O)(OH)] with *n*-$Bu_2SnO$ and (*n*-$Bu_3Sn)_2O$ have been studied. Two novel organotin phosphinates, [{(*n*-$Bu_2Sn)_2$(OH)}{*cyc*$PO_2$}$_3$]$_n$ (**1**) and [(*n*-$Bu_3Sn$)(*cyc*$PO_2$)]$_4$ (**2**), have been isolated in these reactions. Compound **1** is a spirocyclic coordination polymer containing alternate six- ($Sn_2PO_3$) and eight-membered ($Sn_2P_2O_4$) rings. In contrast, compound **2** is a 16-membered macrocycle containing tin, oxygen, and phosphorus atoms. The macrocyclic nature of **2** is retained in chloroform solution up to 2 mM concentration.

## Introduction

Clusters, cages, rings, and coordination polymers containing organooxotin motifs have been of considerable interest in recent years.[1−4] In general, this family of compounds can be prepared either by controlled hydrolysis of organotin halides or by the reactions of appropriate organotin precursors with carboxylic, phosphonic, phosphinic, or sulfonic acids.[1] In particular, the reactions of monoorganotin substrates such as *n*-BuSn(O)OH with phosphorus-based acids have proved to be extremely fruitful. A large number of structurally diverse organooxotin assemblies have been realized by relatively simple synthetic methodologies involving primarily a change of substituents at the phosphorus center.[1] Thus, several novel cages such as *drums*, *cubes*, *O-capped clusters*, *double O-capped cluster*, *tetranuclear cages*, *butterfly clusters*, and *football cages* have been prepared and structurally characterized.[5−11] Recently a solventless methodology for the preparation of some of these clusters has also been reported.[12] In contrast to the reactions of *n*-BuSn(O)OH with phosphorus-based acids, corresponding reactions involving di- and triorganotin precursors have not been studied in such detail.[3b,d−f] It is of interest to explore if structurally diverse products would also be accessible in these systems. Herein, we report our results on the investigations of the reactions of a sterically strained phosphinic acid, viz., 1,1,2,3,3-pentamethyltrimethylene phosphinic acid [*cyc*P(O)OH] with *n*-$Bu_2SnO$ and (*n*-$Bu_3Sn)_2O$. The formation and structural characterization of a novel spirocyclic coordination polymer, [{(*n*-$Bu_2Sn)_2$(OH)}{*cyc*$PO_2$}$_3$]$_n$ (**1**), and a 16-membered macrocycle, [(*n*-$Bu_3Sn$)(*cyc*$PO_2$)]$_4$ (**2**), are reported.

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**Table 1. Crystal and Structure Refinement Data for Compounds 1 and 2**

| | 1 | 2 |
|---|---|---|
| empirical formula | $C_{40}H_{85}O_7P_3Sn_2$ | $C_{80}H_{172}O_8P_4Sn_4$ |
| fw | 1008.37 | 1860.82 |
| temperature | 150(2) K | 150(2) K |
| wavelength | 0.71073 Å | 0.71073 Å |
| cryst syst | monoclinic | tetragonal |
| space group | $P2(1)/c$ | $P4(2)/n$ |
| unit cell dimens | $a = 16.512(3)$ Å, $\alpha = 90°$ | $a = 19.2108(8)$ Å, $\alpha = 90°$ |
| | $b = 17.259(3)$ Å, $\beta = 102.758(4)°$ | $b = 19.2108(8)$ Å, $\beta = 90°$ |
| | $c = 18.228(4)$ Å, $\gamma = 90°$ | $c = 13.0532(7)$ Å, $\gamma = 90°$ |
| volume | 5066.3(17) Å$^3$ | 4817.3(4) Å$^3$ |
| $Z$ | 4 | 2 |
| density (calcd) | 1.322 Mg/m$^3$ | 1.283 Mg/m$^3$ |
| absorp coeff | 1.120 mm$^{-1}$ | 1.136 mm$^{-1}$ |
| $F(000)$ | 2104 | 1952 |
| cryst size | $0.4 \times 0.3 \times 0.16$ mm$^3$ | $0.40 \times 0.35 \times 0.18$ mm$^3$ |
| $\theta$ range for data collection | 1.26 to 25.03° | 1.5 to 25.03° |
| index ranges | $-19 \le h \le 15, -18 \le k \le 20, -21 \le l \le 19$ | $-22 \le h \le 21, -22 \le k \le 18, -10 \le l \le 15$ |
| no. of reflns collected | 23 081 | 25 001 |
| no. of indep reflns | 8938 [$R$(int) = 0.0562] | 4267 [$R$(int) = 0.0272] |
| completeness to $\theta = 25.03°$ | 99.7% | 100% |
| absorp corr | semiempirical from equivalents | semiempirical from equivalents |
| refinement method | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ |
| no. of data/restraint/params | 8938/1/482 | 4267/163/197 |
| goodness-of-fit on $F^2$ | 0.952 | 1.020 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0419, wR2 = 0.0917 | R1 = 0.0449, wR2 = 0.1133 |
| $R$ indices (all data) | R1 = 0.0839, wR2 = 0.1102 | R1 = 0.0627, wR2 = 0.1296 |
| largest diff peak and hole | 1.112 and −1.102 e·Å$^3$ | 0.847 and −0.313 e·Å$^3$ |

## Experimental Section

**General Procedures.** The reactions were performed under a dry nitrogen atmosphere by employing standard Schlenk techniques. Solvents were dried over sodium benzophenone ketyl and were collected from the still at the time of reaction. $n$-$Bu_2SnO$ and ($n$-$Bu_3Sn)_2O$ were purchased from Aldrich and used without further purification. 1,1,2,3,3-Pentamethyltrimethylene phosphinic acid [*cyc*P(O)(OH)] was prepared by employing the literature method.[13] Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE Instruments model EA/110 CHNS-O elemental analyzer. $^1H$, $^{31}P$, and $^{119}Sn$ NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer using $CDCl_3$ solutions with shifts referenced to tetramethylsilane, 85% $H_3PO_4$, and tetramethyltin, respectively. $^{31}P$ and $^{119}Sn$ NMR were recorded under broad-band decoupled conditions. Vapor pressure osmometric studies (in $CHCl_3$) were carried out using a Knauer vapor pressure osmometer model A028.

**X-ray Crystallography.** Crystals of **1** and **2** were grown by slow diffusion of $n$-hexane in dichloromethane at room temperature. Colorless blocklike crystals of **1** and **2** suitable for single-crystal X-ray diffraction were loaded on a Bruker AXS Smart Apex CCD diffractometer. The details pertaining to the data collection and refinement for **1** and **2** are given in Table 1. In **2** the carbon atoms of the butyl groups and the carbon atoms of the phosphorus ligand were disordered. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on $F^2$ using SHELXL-97.[14,15] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

**Synthesis. 1. Preparation of [{($n$-$Bu_2Sn)_2$(OH)}{*cyc*$PO_2$}$_3$]$_n$ (1).** $n$-$Bu_2SnO$ (1.00 g, 4.01 mmol) and *cyc*P(O)(OH) (0.70 g, 4.01 mmol) were refluxed in toluene (80 mL) for 6 h. A Dean−Stark apparatus was used to facilitate the dynamic removal of the water formed in the reaction by azeotropic distillation. The reaction mixture was allowed to attain room temperature and filtered. The filtrate was stripped of the solvent in vacuo to obtain a white solid. This was recrystallized from dichloromethane and $n$-hexane (1:1) at room temperature to afford crystals of compound **1**. Yield: 1.11 g (55%). Mp: 166 °C. Anal. Calcd for $C_{40}H_{85}O_7P_3Sn_2$: C, 47.64; H, 8.49. Found: C, 47.34; H, 8.31. $^1H$ NMR ($CDCl_3$, ppm): 0.75 (d), 0.85 (t), 1.05 (t), 1.18−1.67 (m). $^{31}P$ NMR ($CDCl_3$, ppm): 51.7 (s), 48.1 (s). $^{119}Sn$ NMR ($CDCl_3$, ppm): −187.2.

**2. Preparation of [($n$-$Bu_3Sn$)(*cyc*$PO_2$)]$_4$ (2).** ($n$-$Bu_3Sn)_2O$ (2.34 g, 3.92 mmol) and *cyc*P(O)(OH) (1.38 g, 7.85 mmol) were reacted in a manner similar to that described for the previous preparation to afford the product as a white solid. Crystals of **2** were obtained from dichloromethane and hexane (1:1, slow diffusion) at room temperature in 2−3 days. Yield: 3.12 g (85%). Mp: 204 °C. Anal. Calcd for $C_{80}H_{172}O_8P_4Sn_4$: C, 51.63; H, 9.31. Found: C, 51.21; H, 9.13. Molecular weight: 1860 (2.0 mM); 465 (0.5 mM). $^1H$ NMR ($C_6D_6$, ppm): 0.48 (d), 0.85 (s), 0.91−1.09 (m), 1.13−1.51 (m), 1.77 (s). $^{31}P$ NMR ($C_6D_6$, ppm): 36.0 (s). $^{119}Sn$ NMR ($C_6D_6$, ppm): −86.2 (s).

## Results and Discussion

**Synthetic Aspects.** The reaction of $n$-$Bu_2SnO$ with *cyc*P(O)OH in a 1:1 stoichiometric ratio in boiling toluene for 6 h affords predominantly the product [{($n$-$Bu_2Sn)_2$(OH)}{*cyc*$PO_2$}$_3$]$_n$ **1** (Scheme 1). Removal of water from the reaction mixture was effected by the use of a Dean−Stark apparatus. The $^{119}Sn$ NMR of **1** showed the presence of a signal at −187.2 ppm characteristic of a $C_2O_4$ coordination environment around tin.[16] The $^{31}P$ NMR spectrum of **1** showed two signals at 51.7 and 48.1 ppm, indicating the presence of two types of phosphinate ligands.

The reaction of ($n$-$Bu_3Sn)_2O$ with *cyc*P(O)(OH) in a 1:2 stoichiometry leads to the formation of [$n$-$Bu_3$-

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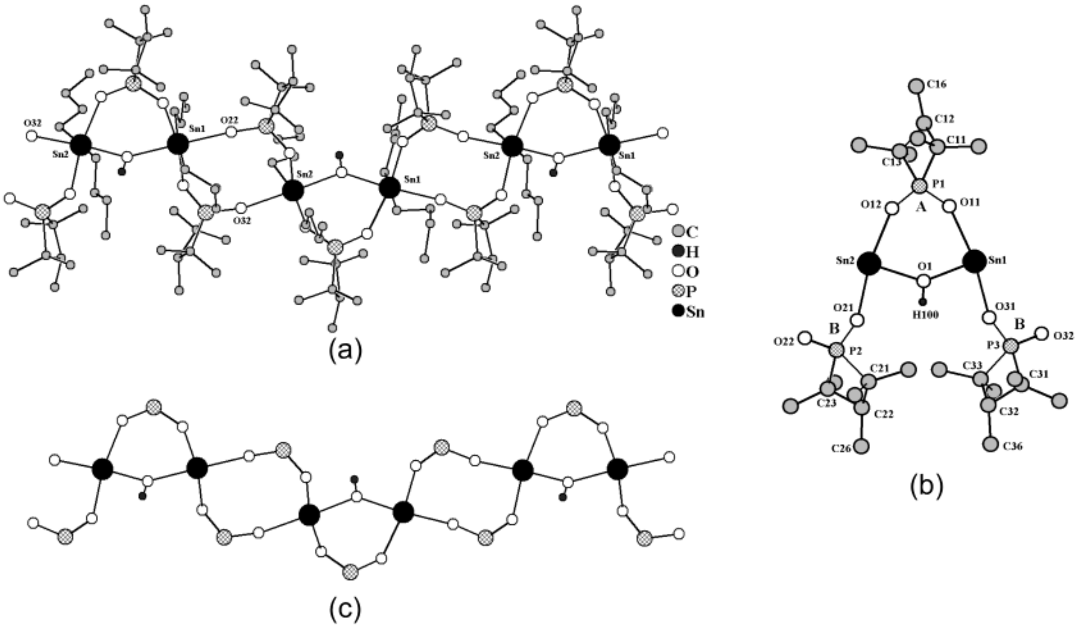
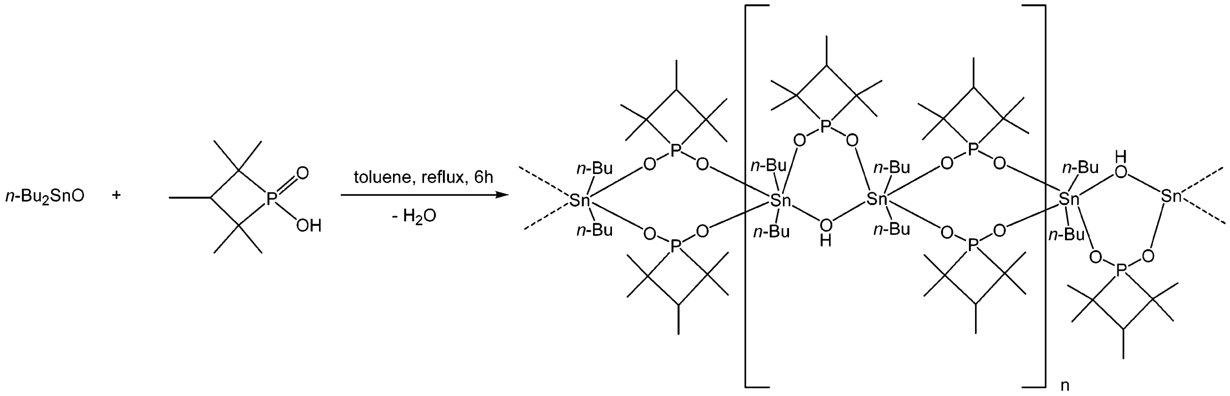


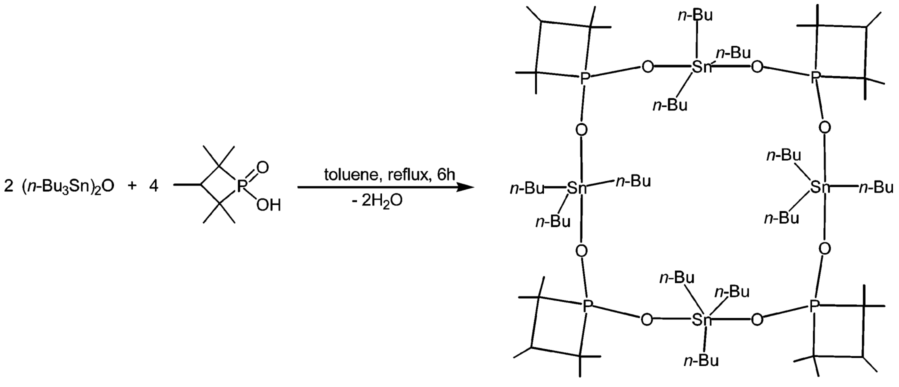
**Figure 1.** (a) Molecular structure of [{($n$-Bu$_2$Sn)$_2$(OH)}{*cyc*PO$_2$}$_3$]$_n$, **1**. (b) Structure of the asymmetric unit of **1**. (c) Sn−O−P core of **1** showing the presence of alternate six- and eight-membered rings.

**Scheme 1**



**1**

**Scheme 2**



**2**

SnO$_2$P*cyc*]$_4$ (**2**) (Scheme 2). The $^{119}$Sn NMR of **2** shows a signal at −85.2 ppm, while a signal at 36.0 ppm is seen in its $^{31}$P NMR spectrum. The organotin phosphinates **1** and **2** were found to be present in polymeric and macrocyclic structures, respectively.

**X-ray Crystal Structures of 1 and 2.** The molecular structure of the coordination polymer **1** is shown in Figure 1a. Selected metric parameters for **1** are given in Table 2. The asymmetric unit of the polymer consists of a ditin center connected through a hydroxy bridge (Figure 1b). This unit contains three phosphinate ligands (labeled A and B in Figure 1b) bound to the tins in two different coordination modes. Phosphinate A binds the two tin centers Sn1 and Sn2 across the

**Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1**

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Sn2−O1 | 2.184(4) | P1−O11 | 1.524(4) |
| Sn2−O12 | 2.252(4) | P1−O12 | 1.539(4) |
| Sn2−O21 | 2.211(3) | P2−O21 | 1.544(4) |
| Sn2−O32 | 2.307(4) | P2−O22 | 1.509(4) |
| Sn2−C205 | 2.155(5) | P3−O31 | 1.540(4) |
| Sn2−C201 | 2.161(5) | P3−O32 | 1.517(4) |
| Sn1−O1 | 2.197(4) | O1−H100 | 0.814(3) |
| Sn1−O11 | 2.269(3) | Sn1−O22 | 2.288(4) |
| Sn1−O31 | 2.203(3) | Sn1−C101 | 2.154(5) |
| Bond Angles | | | |
| Sn2−O1−Sn1 | 141.02(18) | O12−Sn2−O32 | 95.78(13) |
| O21−Sn2−O12 | 169.47(13) | O1−Sn1−O31 | 82.38(13) |
| O32−Sn2−O1 | 176.72(13) | O31−Sn1−O22 | 93.68(13) |
| C201−Sn2−C205 | 169.49(19) | O11−Sn1−O1 | 87.11(13) |
| O32−Sn2−O21 | 94.73(12) | C101−Sn1−C105 | 170.52(19) |
| O21−Sn2−O1 | 82.03(13) | O12−P1−O11 | 116.25(20) |
| O1−Sn2−O12 | 87.45(13) | O22−P2−O21 | 116.00(20) |
| O31−P3−O32 | 116.79(21) | P1−O12−Sn2 | 135.47(21) |
| P1−O11−Sn1 | 140.77(21) | P2−O21−Sn2 | 137.57(21) |
| P3−O31−Sn1 | 143.08(22) | P2−O22−Sn1 | 166.11(22) |
| P3−O32−Sn2 | 156.83(22) | | |

hydroxy bridge, resulting in the formation of a six-membered $Sn_2PO_3$ heterocyclic ring. On the other hand the phosphinates labeled B are involved in bridging adjacent ditin motifs. This results in the formation of an eight-membered $Sn_2P_2O_4$ heterocycle. The cumulative effect of the two types of bridging coordination of the phosphinates A and B is the formation of an unusual coordination polymer containing alternate six- and eight-membered rings with each tin center being the *junction* of the spirocyclic ring systems. Each tin is six-coordinate with a $C_2O_4$ coordination environment. The geometry around each tin is approximately octahedral, where the two alkyl groups occupy the trans positions.

Two sets of P−O distances are encountered in the coordination polymer **1**. The phosphinates labeled A have shorter P−O distances (1.524(4) and 1.539(4) Å) compared to the phosphinates labeled B (1.544(4) and 1.540(4) Å). In comparison, the Sn−O distances arising out of ligation with phosphinates labeled A are longer (2.252(4) and 2.269(3) Å) than the corresponding distances arising out of interaction with phosphinate B (2.211(3) and 2.203(3) Å). The oxygens O22 and O32 (Figure 1b) of the phosphinates labeled B that are responsible for the formation of the coordination polymer also are involved in the longest Sn−O distances seen in **1**, viz., 2.288(4) and 2.307(4) Å. In contrast the corresponding P−O distances are the shortest (1.509(4) and 1.517(4) Å).

The Sn−O−P core of the coordination polymer possessing alternating six- and eight-membered rings is shown in Figure 1c. Both the six- and the eight-membered rings are almost planar. The mean plane deviations of the atoms in these rings are 0.13 and 0.17 Å, respectively. Adjacent six- and eight-membered rings are nearly coplanar; thus, the dihedral angle between the mean planes formed by these two rings is 5.3°.

It is interesting to compare the structure of **1** with existing Sn−O rings and polymers arising from diorganotin motifs. Common structural forms containing the diorganotin/carboxylate motifs include the ladder structures containing tetranuclear tin assemblies built from a $Sn_2O_2$ core.[17] On the other hand the structure of $[(n\text{-}Bu_2Sn)_2(OH)(O_2CCCl_3)_3]$ (formed in the reaction of $n$-$Bu_2SnO$ with trichloroacetic acid) contains a ditin motif bridged by a hydroxide and a $\mu$-2 carboxylate.[18] Two other carboxylates present in this compound are found to coordinate in a monodentate manner (Figure 2a). Eight-membered ring formation containing a ditin unit and two bridging phosphonates has been found recently for $[n\text{-}Bu_2Sn\{MePO_2(OH)\}\{MeP(O)(OH)O\}]_2$ (Figure 2b).[19] Uniquely, compound **1** combines both these structural motifs and represents an unprecedented example (Figure 2c). This is made possible by the $\mu$-2 bridging coordination mode of *all* the phosphinates present in this molecule.

The molecular structure of **2** is shown in Figure 3 (a and b). Selected metric parameters for this compound are summarized in Table 3. Compound **2** is a 16-membered $Sn_4P_4O_8$ inorganic macrocycle formed by the intermolecular linkage of four $n$-$Bu_3Sn$ units. Thus, adjacent triorganotin motifs are bridged by the phosphinate ligand *cyc*$PO_2$ via a $\mu$-2 coordination mode to afford an approximate *molecular square* (Figure 3b).

Each tin is trigonal bipyramidal ($C_3O_2$ coordination environment), with the apical positions being taken up by the oxygen atoms of two different phosphinate ligands. The apical O−Sn−O angle is almost linear (average: 176.2(14)°). Two types of tin oxygen bond distances are seen (cf. Sn1−O1, 2.268(4) Å; Sn1−O8, 2.209(4) Å), reflecting a slight anisobidentate nature of binding by the phosphinate ligand. This is also seen in the small variation of the P−O distances within a phosphinate ligand [1.485(4) and 1.503(4) Å]. Finally, the macrocycle is characterized by the presence of alternate linear and bent Sn−O−P units (cf. Sn1−O1−P1, 175.99°; Sn1−O8−P4, 152.54°). The macrocyclic ring is slightly puckered, as evidenced by an average deviation of 0.25 Å by the constituent atoms from the mean plane of the ring. Although there has been molecular weight evidence for the tetrameric 16-membered inorganic macrocyclic rings in triorganotin phosphinates,[20] prior to the present example, there has been only one other that has been characterized by crystallography.[21]

Vapor pressure osmometric studies have been carried out on **2** to find out if the tetrameric structure is retained in solution as well. From these studies, in chloroform solution, it is revealed that up to a limiting solution concentration of 2 mM the tetrameric nature of the macrocycle is retained. On decreasing the concentration to 0.5 mM, dissociation of the macrocycle was noticed and it remained largely a monomer. Interestingly, it is to be noted that $Me_3SnO_2PPh_2$ also retains its 16-membered macrocycle character in solution.[21] In contrast, the corresponding $n$-$Bu_3SnO_2C$-$C_6H_3$-2,6-$F_2$, which also shows a 16-membered structure in the solid state, disintegrates into a monomer in solution.[22] A comparison of the Sn−O bond distances of **2** with those of $Me_3SnO_2PPh_2$ and $n$-$Bu_3SnO_2C$-$C_6H_3$-2,6-$F_2$ reveals

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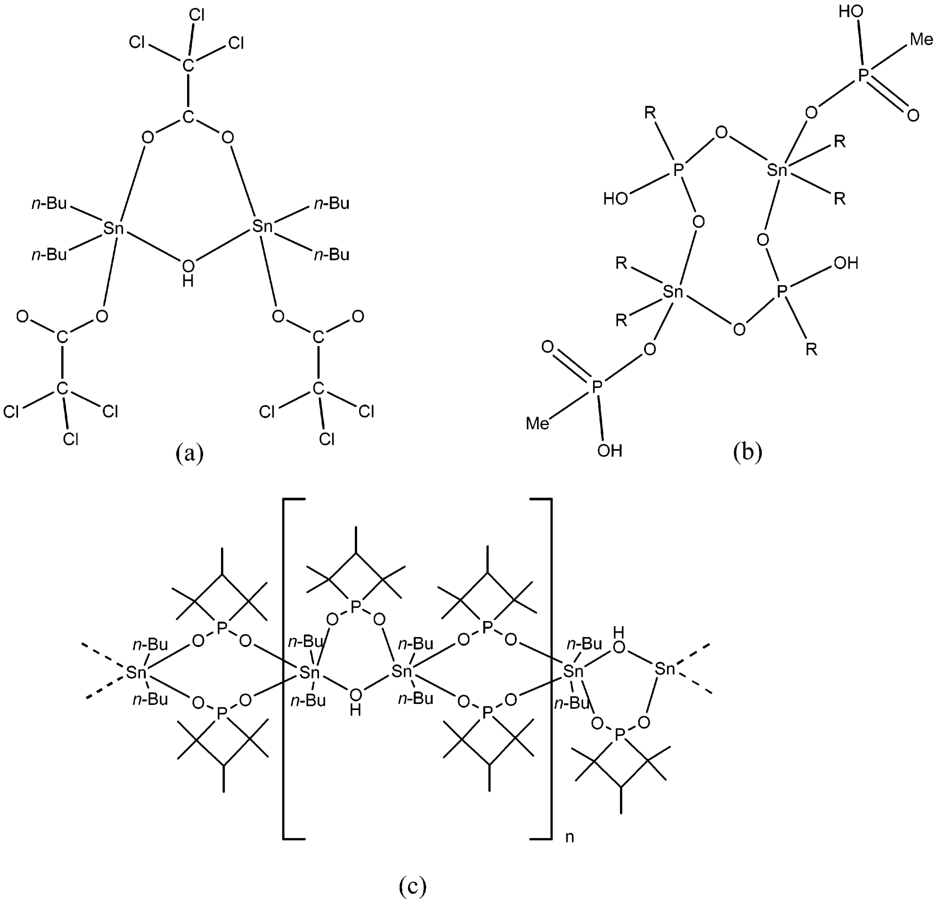

**Figure 2.** Structural comparisons of [$(n\text{-}Bu_2Sn)_2(OH)(O_2CCCl_3)_3$] (a) and [$n\text{-}Bu_2Sn(HO_3PMe)_2]_2$ (b) with **1c**.

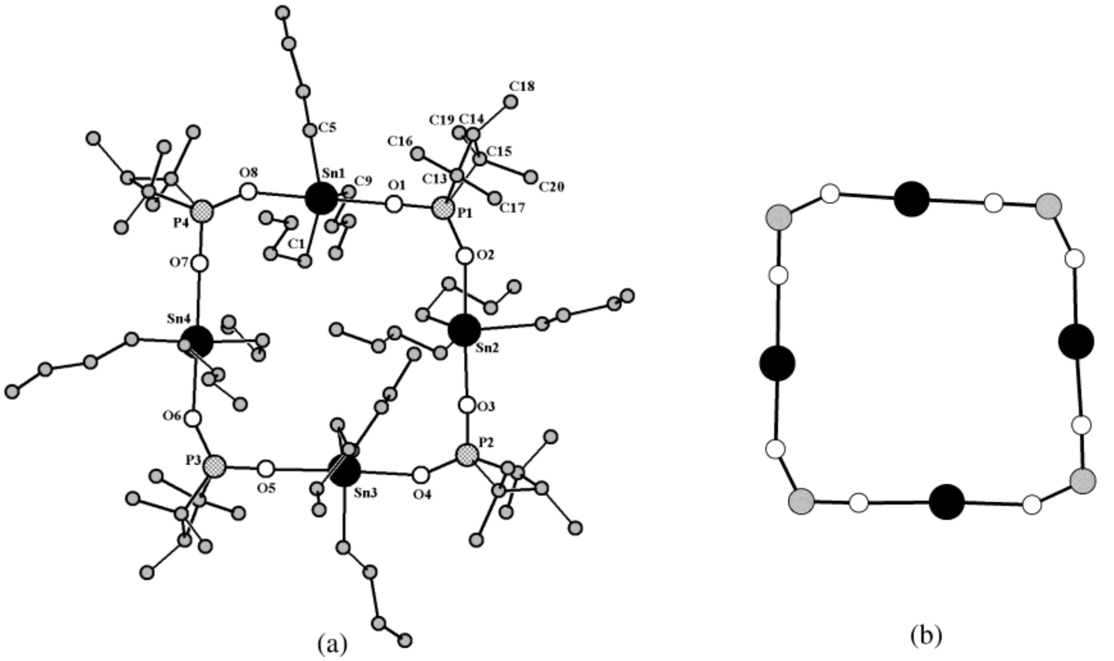

**Figure 3.** (a) Molecular structure of [$(n\text{-}Bu_3Sn)(cycPO_2)]_4$, **2**. (b) View of the 16-membered Sn−O−P macrocycle.

that while in the latter the difference in the two Sn−O bond distances is considerable [(2.186(4) and 2.514(4) Å: *d*(Sn−O), 0.328 Å)], in the former [{2.268(4) and 2.209(4) Å; *d*(Sn−O), 0.059 Å for **2**}{(2.243(5) and 2.245(6) Å; *d*(Sn−O), 0.002 Å for $Me_3SnO_2PPh_2$}] the Sn−O distances are nearly identical. This suggests that the relatively symmetric coordination mode of the phosphinate in **2** allows the retention of the macrocyclic structure in solution at least up to 2 mM concentration.

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**Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2**

| Bond Lengths | | Bond Angles | |
|---|---|---|---|
| Sn1−O1 | 2.268(4) | O1−Sn1−O8 | 176.20(14) |
| Sn1−O8 | 2.209(4) | C1−Sn1−C5 | 118.81(40) |
| Sn1−C1 | 2.115(6) | C1−Sn1−C9 | 126.70(29) |
| Sn1−C9 | 2.178(9) | C5−Sn1−C9 | 114.48(50) |
| Sn1−C5 | 2.232(14) | Sn1−O1−P1 | 175.99(24) |
| P1−O1 | 1.485(4) | Sn1−O8−P4 | 152.54(24) |
| P1−O2 | 1.503(4) | | |

## Conclusion

In conclusion by the use of a sterically hindered phosphinc acid where phosphorus is part of a four-membered ring we have been able to synthesize a novel spirocyclic coordination polymer containing a diorganotin structural unit. On the other hand the reaction of this phosphinic acid with a triorganotin precursor leads to the assembly of a 16-membered inorganic macrocycle.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

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